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<p>(54) Title: METHOD AND APPARATUS FOR ENRICHING VOLATILE SUBSTANCE (VOLATILE SUBSTANCES) FROM A GAS STREAM AND METERING THE SUBSTANCE OR SUBSTANCES TO AN ANALYTICAL INSTRUMENT</p> <p>(57) Abstract</p> <p>The present invention relates to a method of enriching a volatile substance or volatile substances from a gas flow that has already been generated and metering the volatile substance(s) to an analytical instrument in a limited gas flow, characterized by either sucking or pressing the gas flow via a first switching valve to an adsorber in which the volatile substance or volatile substances is/are adsorbed, and causing the gas flow freed from said substance or substances to leave the system via at least said first switching valve; causing a controlled amount of inert gas to flow via the first switching valve to the adsorber, which is heated with the aid of an infusion pump and through said adsorber while taking up the volatile substance or volatile substances, again via the first switching valve and via a second switching valve to the infusion pump; and delivering the inert gas together with its volatile substance or volatile substances content to the analytical instrument via said infusion pump and said second switching valve. The present invention also relates to apparatus for carrying out the method.</p>			

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Method and apparatus for enriching volatile substance (volatile substances) from a gas stream and metering the substance or substances to an analytical instrument

Technical field

The invention relates to a method and to an apparatus for enriching a volatile substance or substances from a gas stream and metering the substance or substances to an analytical instrument.

There is an interest in many industrial areas to establish the presence of volatile substances, often organic substances, that are released by or that surround a product and also the quantities in which such substances are present. Substances that are odorous and/or have a taste-giving effect are of pronounced interest in this regard. In the case of the manufacture and further development of packaging materials, such as paperboard and paper, endeavors are made to ensure that the packaging material will neither be odorous nor convey any taste to the packaged object, for instance different kinds of foodstuffs. Both the manufacturer and converter of such material wishes to be able to establish whether or not the material concerned gives off any volatile substances that are odorous and/or have a taste-giving effect, and if so in what quantities or concentrations.

Substances that are odorous and/or have a taste-giving effect are of interest in the manufacture of perfumes, other fragrant products, tobacco and foodstuffs.

Some volatile substances are harmful in different ways and even toxic, and it is of interest to be able to analyse such substances even though they may not smell. When different products are painted and lacquered, such as cars, the product will be enveloped by a large amount of volatile substances.

There is an interest in a large number of laboratories within widely different fields to be able to analyse different gas samples that contain volatile substances, normally organic substances.

The aforesaid substances are either already initially present in a gaseous state, normally in the surrounding air, or are caused to transform to a gaseous state, normally in the surrounding air, in exceedingly low amounts or concentrations. In order to be able to determine the concentrations of such substances concerned, there is a serious need of being able partly to enrich the volatile substances of interest in the gas sample, which is normally taken from the surrounding air, and partly to meter the volatile substances in a limited gas volume to an analytical instrument. The present invention is suitable for application within this technical field.

Background art

As will be apparent from the foregoing stated, there are situations where the volatile substances, often odorous substances and/or substances that have a taste-giving effect, are already initially in a gaseous state in mixture normally with air. There are other situations in which volatile substances are present in a solid product and which are emitted from the product to a limited extent and/or at a

low rate, for instance at room temperature. In such circumstances, the solid material is often heated, so as to displace the physical equilibrium of the volatile substances towards the gas phase.

5 The gas mixture intended for analysis is designated in the art as headspace gas and can be generated in many different ways, none of which will be described in this document.

10 As before mentioned, the concentration of those volatile substances of interest in such gas volumes is extremely low. For instance, the water vapour content of the gas volume or gas sample is often several thousand times greater than the volatile substance content, particularly when heating a solid material in order to increase the 15 emission of volatile substances.

20 The presence of water vapour causes serious problems in some analytical processes, at least when present in high concentrations, therewith making it necessary to radically reduce the amount of water vapour present in the sample.

25 One way of achieving this is to pass the gas sample through a tube made of water-permeable polymeric material. However, it has been found that this method not only removes water vapour from the gas sample but that a part of the volatile substances may also be removed. In addition, the gas sample may be contaminated by the polymeric material. Another way of extracting the water vapour content is to freeze out 30 the water vapour as ice, for instance at a temperature of -10°C to -20°C. It has been found that pure ice will not adsorb volatile organic substances. Despite this, some less volatile substances can be lost from the gas volume or gas sample in the freezing out process.

A requirement of certain analytical methods is that the gas volume or gas sample is free from oxygen, in which

case oxygen must be removed from the gas sample. Other analytical methods require the presence of a certain amount of oxygen in the gas volume or the gas sample, in which cases there is usually added to the gas sample a controlled amount 5 of oxygen containing gas.

In order to enrich volatile substances from a given gas quantity it is known to adsorb the substances concerned on an adsorbent and thereafter release the substances from the adsorbent by heating the same, so-called thermal 10 desorption.

In this case, a compromise must always be made between the yield of volatile substances and the elimination of water vapour from the resultant gas sample. The volatile substances are enriched by allowing the substances to be 15 taken up in a smaller quantity of gas, normally an inert gas, than the amount of gas present in the original sample, in the desorption process.

In order for the analysis of the volatile substances in a gas sample to be successful, even when the 20 concentration of volatile substances is, i.e. has been caused to be, sufficiently high to enable a measuring process or determining process to be effected, the gas sample must be metered to and into the analytical instrument in a controlled manner, including a uniform gas flow over a given period of 25 time.

Disclosure of the invention

Technical problem

As will be apparent from the foregoing stated, it is often difficult to ascertain the presence of a volatile 30 substance in a gas sample and to determine the concentration of said substance in said sample, among other things because of the exceedingly small substance concentration in the sample. Furthermore it is difficult to meter the gas sample

to and into the analytical instrument in a sufficiently controlled manner. In other words, there is a need for a method (and an apparatus) which prepares the gas samples with their contents of volatile substance or volatile substances on one hand and which delivers the gas samples to the analytical instrument in an enduringly successful and reliable manner on the other hand.

The solution

The present invention provides a solution to that and relates to a method for enriching a volatile substance or volatile substances from a gas flow that has already been generated, and metering the volatile substance or volatile substances to an analytical instrument in a limited gas quantity, wherein the method is characterized in that the gas flow is either sucked or pressed via a first switching valve to an adsorber in which the volatile substance or volatile substances is/are adsorbed and the gas flow freed from said substance or substances is caused to leave the system via at least said first switching valve; in that a controlled amount of inert gas is caused to flow with the aid of an infusion pump (aspiration) to said adsorber, which is heated, via said first switching valve and through said adsorber (thermal desorption) while taking up the volatile substance or volatile substances, again via the first switching valve and via a second switching valve, to the infusion pump; and in that the inert gas and its volatile substance content is delivered to the analytical instrument via said infusion pump (injection) and the second switching valve.

The inventive method is adapted for all analytical methods known in the described context. For instance, the presence of a volatile substance or volatile substances in the sample and the concentration of said substance or

substances can be determined by gas chromatography, infrared spectroscopy, and with sensors, so-called electronic noses.

5 If, in order to carry out a successful analysis, it is necessary to free the gas stream from a smaller or larger part of its water vapour content, this is effected in a first, initial treatment stage by refrigeration drying.

10 If no oxygen whatsoever may be present in the thermal desorption process or thereafter, an inert gas is caused to flow through the adsorber prior to heating the same, so that any oxygen present is displaced and the inert 15 gas containing said oxygen is caused to leave the system via at least the first switching valve.

20 In some cases the analytical method requires the presence of oxygen, in which case an oxygen-containing gas, for instance air or oxygen, is supplied in a controlled quantity to the limited gas quantity (the sample) immediately upstream of the analytical instrument or in said instrument.

Any known, appropriate inert gas can be used as a carrier gas. Helium and nitrogen are the gases most 25 preferred.

The inventive method can be applied with analyses carried out in a laboratory and in analytical processes carried out in the production of different products, so-called on-line measurements.

25 When the analysis is carried out with the aid of sensors, so-called electronic noses, preparation of the sample is particularly sophisticated, since it is necessary to greatly reduce the water vapour content of the gas stream already generated and since a given controlled amount of 30 oxygen must be present in the gas sample during the analysis.

The invention also relates to an apparatus for enriching a volatile substance or volatile substances from a gas flow that has already been generated, and metering the volatile substance or volatile substances to an analytical

instrument in a limited gas quantity, characterized in that the apparatus includes a first gas flow circuit which comprises conduits, a first switching valve, a heatable adsorber in which the volatile substance or volatile substances is/are adsorbed, an outlet for cleansed gas flow, and means for driving the gas flow through the flow circuit, a second flow circuit for a limited quantity of inert gas which functions as a vehicle for the volatile substance or the volatile substances and which includes a regulating unit for the inert gas and other gas, conduits, said first switching valve, the heated adsorber functioning as a desorber, a second switching valve, and an infusion pump that drives the inert gas through the flow circuit, and a third flow circuit for delivering the inert gas and its volatile substance or volatile substances content to the analytical instrument comprising conduits, the second switching valve and said infusion pump.

The combined adsorber/desorber is an important part of the apparatus.

The combined adsorber/desorber is normally tubular in shape and made, for instance, of glass or steel. In some cases, the inner surface of the tube is treated so that no substance that can disturb preparation of the sample or the following analysis can escape. The inner surface can be said to be inert. The adsorbent, i.e. the chemical concerned, may be any known adsorbent. Examples of such adsorbents are active charcoal, a substance retailed under the designation Tenax (which is chemically poly-2,6-diphenyl-p-phenylene oxide), and a substance which is retailed under the designation HayeSep Q (which chemically is a copolymer of styrene and divinyl benzene). The adsorber/desorber includes a heating device, for instance an electric filament which is embodied in the tube material or is wound on the outside of the tube. The tube may also be surrounded by metal plates in

the form of so-called Peltier elements. These elements enable the temperature to be lowered and raised within the tube in relation to ambient room temperature.

5 The switching valves are another important part of the apparatus. Any known switching valve can be used.

Switching valves that have different numbers of inlets and outlets, referred to as ports, are commercially available.

10 These valves may contain ten, eight and four ports. The number of ports required in the switching valves used in the present case is at least partially dependent on the analytical instrument to which the inventive apparatus is connected. Certain analytical methods and analytical instruments require more sophisticated sample preparation than others and the requirement for a given port number is contingent thereon.

15 As earlier mentioned, the gas stream that has already been generated, i.e. the original gas stream, is sucked or pressed through the first flow circuit, therewith requiring the presence of a device to this end. This device may comprise a pump, which is preferably applied in the 20 external analytical instrument or at the conduit that extends out from said instrument. Some analytical instruments will include a pump, which is then used for the work described. In the described case, the gas stream is sucked through the flow circuit or, in a particular case, through the flow circuits 25 (see below). The pump mentioned can be placed at a number of positions, for instance at the inlet conduit to the external analytical instrument or connected to or adjacent to the conduit immediately downstream of the first switching valve. The device, e.g. pump, may alternatively be placed adjacent 30 the conduit that extends into and is connected to the inventive apparatus, in which case the gas stream is pressed through the flow circuit or circuits.

It is often necessary to supplement the apparatus with an initial flow circuit for removing water vapour from

the gas stream, or the so-called headspace gas, this circuit including conduits, an initial switching valve, at least one refrigeration drier and the aforesaid device that drives the inert gas through the initial flow circuit.

5 A preferred refrigeration drier is one that includes one or more Peltier elements. A particular feature of such elements is that the element becomes cold when an electric current passes along a certain route through the element, while passage of the current in the reverse 10 direction results in heating of said element. The temperature in the drier can be varied between -30°C and +55°C. The major part of the water vapour in the gas stream is frozen out in the refrigeration drier in the form of ice, at a temperature of about -15°C.

15 This embodiment of the apparatus that includes an initial flow circuit for removing water vapour from the gas stream includes an inlet conduit and a regulating unit, for the delivery of cleansing gas, for instance air, and an outlet conduit for the removal of water condensate and/or 20 water vapour from the refrigeration drier and the flow circuit subsequent to the treatment of the gas stream. Subsequent to the original gas stream and its volatile substance content leaving the initial flow circuit, the refrigeration drier is heated so as to melt the ice that has 25 formed. At the same time, cleansing air is passed through a conduit from the regulating unit to the switching valve, through said valve and through the refrigeration drier back to the switching valve and out to the apparatus surroundings via said switching valve. The mentioned cleansing air 30 entrains the water and/or the water vapour formed by the molten ice and the initial flow circuit is therewith cleansed and ready to receive a fresh gas sample with its content of volatile substance or volatile substances.

According to one embodiment of the invention, the apparatus includes regulating unit and conduit for delivering oxygen-containing gas, with said conduit discharging into the conduit that is connected to the analytical instrument, or 5 discharging into the analytical instrument itself.

A central unit of the inventive apparatus is the reciprocating infusion pump. Any appropriate known kind of pump can be used. A preferred type of infusion pump is one which comprises essentially a cylinder and a piston or plate 10 which is sealingly mounted in the cylinder and attached to a rod. The rod enables the piston to be moved reciprocatingly in the cylinder. By selecting a cylinder of given volume, it is possible to determine the amount of inert gas in which the volatile substance or volatile substances has/have been taken 15 up during the thermal desorption process, and therewith also the amount of gas introduced into the analytical instrument. Such an infusion pump will also enable the gas flow to be readily controlled into the analytical instrument, for instance at a constant rate.

20 **Advantages**

One advantage afforded by the inventive method and apparatus is their flexibility. As earlier mentioned, the presence and concentration of, for instance, an odorous volatile substance in a gas sample can be determined in 25 different ways. Sample preparation may differ with different analytical processes, and because the inventive method comprises a number of more or less independent steps and the inventive apparatus comprises a number of more or less independent flow circuits, the method and apparatus may be 30 tailor-made to suit respective analytical process.

Because both the desorption process and the metering process are controlled through the medium of an infusion pump and its aspiration and injection respectively,

several advantages are afforded. One of these advantages resides in the ease in which the extent to which the volatile substance is enriched can be controlled. When the quantity of the original gas sample is known, the required quantity of 5 inert gas in which the volatile substance is taken up in the thermal desorption can be chosen, by means of the size or the volume of the infusion pump, and thereby limit the gas quantity delivered to the analytical instrument to the desired extent. This reduction in gas quantity is in direct 10 proportion to the increase in the concentration of the volatile substance, i.e. to the degree of enrichment. Another advantage resides in the ease in which the gas sample can be introduced into the analytical instrument at a constant rate 15 of flow, with the aid of the infusion pump. This is a prerequisite for successful analysis in the case of certain analytical processes.

Description of the drawing

Figure 1 illustrates a preferred embodiment of the inventive apparatus.

20 Best embodiment

A preferred embodiment of the apparatus according to the invention will now be described with reference to Figure 1 in relative detail. Naturally, a preferred embodiment of the inventive method will be described in 25 parallel with this description. Alternative methods and apparatuses according to the invention will also be described to some extent in conjunction therewith. An example as to how the invention can be applied will also be given.

The apparatus set-up illustrated in Figure 1 is 30 connected to an external analytical instrument 1 in the form of a so-called electronic nose, the sensors of which place special requirements on the composition of the gas sample and

the gas flow in the form of a constant oxygen content, low water content and constant flow rate, for instance.

The sample gas whose volatile substance content is to be determined is delivered to the system in a given quantity through the conduit 2. (Here and in the following description only one volatile substance is taken into account for the sake of simplicity and clarity, although in reality the gas will normally contain several volatile substances.) The gas is passed to the initial switching valve 3 via the conduit 2, and from there through the conduit 4 to the refrigeration drier 5. This refrigeration drier includes Peltier elements, the modus operandi of which has earlier been described. The gas is passed back to the initial switching valve 3, through the conduit 6. As the gas is passed through the refrigeration drier 5, it is relieved of the major part of its water vapour content. The gas is passed from the initial switching valve 3 to the first switching valve 8, through the conduit 7, and from there to the adsorber/desorber 10, through the conduit 9. A suitable construction of the adsorber/desorber 10 and its content, i.e. active chemical content, has been earlier described. In this position of the apparatus, the gas is then passed back to the first switching valve 8, through the conduit 11. The gas is passed through the conduit 12 to a second switching valve 13 via said first switching valve 8, and through the conduit 14 to the external analytical instrument 1 via said second switching valve 13. A pump will normally be incorporated in the analytical instrument 1 (not shown in the drawing), and this pump is used in accordance with the above. The gas is not analyzed in this position in the apparatus, but passes straight through the analytical instrument 1 and is caused to leave the system via the outlet conduit 15.

The gas that leaves the system is the original sample gas minus the volatile substance and minus the major

part of the water vapour. Remaining in the system is that which is of the greatest interest in this context, namely the volatile substance stored in the adsorber 10. Also remaining in the system, more specifically in the refrigeration drier 5 5, is the ice, which is later caused to leave the system in the manner described below.

If the analytical instrument 1 does not include a pump, a pump is suitably connected to the outlet conduit 15 (not shown in the drawing).

10 It is important to note that the infusion pump 16 is inoperative during the aforescribed sequence of events.

Since the analysis in the instrument 1 requires a constant oxygen content in the gas sample as the sample passes through the instrument 1 and analysis takes place, it 15 is often necessary to relieve the system concerned, and particularly the adsorber 10, of its oxygen content, said oxygen deriving from the stream of sample gas whose chief constituent is air.

This process step is called the inerting step and 20 is carried out by passing an inert gas, such as helium, from the regulating unit 17 to the first switching valve 8 through the conduit 18, and through said first switching valve 8 to the adsorber 10 via the conduit 11, and from said adsorber back to the first switching valve 8 through the conduit 9 and 25 is then discharged from the system through the conduit 19. This brief stream of inert gas "rearwards" through the described system results in the oxygen present in the system, and then particularly the oxygen in the adsorber 10, being displaced out into the surroundings.

30 An inert gas, such as helium, is supplied to the regulating unit 17 through the conduit 20, and an oxygen-containing gas, such as air, is supplied to said unit through the conduit 21.

It is possible to mix these two gas streams together in the regulating unit. Means for driving the inert gas through the described flow circuit is also required.

As the aforescribed inerting process takes place, 5 heating of the refrigeration drier 5 is started so as to melt the ice present therein. Possibly with some delay, cleansing gas, such as air, is passed from the regulating unit 17 through the conduit 22 to the initial switching valve 3, through said valve 3 and through the conduit 6 to the 10 refrigeration drier 5 and, through the conduit 4, back to the switching valve 3, through said valve and then the gas is passed through the conduit 23 and out into the surroundings. This backward air flushing process frees the refrigeration drier 5 and other involved parts of the flow circuit from the 15 molten ice, in the form of water and/or water vapour. This process also requires some form of means for driving the air through the described flow circuit. It will be noted that the aforesaid can be carried out independently of the remainder 20 of the method, immediately the refrigeration drying is not used.

The infusion pump 16 is inoperative also during the aforescribed inerting stage.

The next phase in the method is the desorption phase. The desorption phase includes initiating heating of 25 the adsorber/desorber 10. The use of the infusion pump 16 is introduced in this stage of the process. More particularly, the infusion pump comprises a cylinder 24, a piston 25 mounted sealingly in said cylinder, and a piston rod 26. The piston 25 is shown slightly spaced from the upper wall of the 30 cylinder 24 in Figure 1. When desiring to utilize the total volume of the infusion pump 16, for instance, the piston 25 is placed in abutment with said upper wall. When the piston 25 is drawn downwards by the piston rod 26 (aspiration), helium is sucked from the regulating unit 17 through the

conduit 18 and to the first switching valve 8 and from there through the conduit 11 to the desorber 10 and passes through said desorber and back to the first switching valve 8 via the conduit 9 and from there to the second switching valve 13. 5 through the conduit 27 and from there through the conduit 28 to the cylinder 24. The amount of inert gas caused to flow through the flow circuit is determined by the distance at which the piston 25 is finally positioned in the cylinder 24. As the inert gas passes through the heated chemical bed in 10 the desorber 10, it entrains the released volatile substance, i.e. the sample molecules, which finally ends up in the cylinder 24. Subsequent hereto, the volatile substance of interest, i.e. the sample molecules, will be present in the cylinder 24 in a considerably smaller gas volume than the 15 original sample gas volume.

The next phase in the method is the metering phase and the analytical operation connected therewith. In this stage of the process, the analytical instrument 1 is supplied with a dry mixture of helium and air through the conduit 29, 20 with a desired oxygen content, and said gas mixture flows through the instrument. Because the sample gas present in the cylinder 24 is totally free of oxygen, the amount of oxygen necessary for carrying out the analysis is controlled by the mixing ratio of air to helium in the conduit 29. The piston 25 rod 26 of the infusion pump 16 is moved up and therewith presses the sample gas (injection) through the conduit 28 to the second switching valve 13 and through said valve and into the analytical instrument 1 through the conduit 14, said 30 sample gas passing through said instrument whilst measuring the concentration of the volatile substance or sample molecules. The sample gas is introduced into the analytical instrument at a controlled and even rate of flow, by moving the piston rod 26 upwards at a controlled and uniform speed.

The analysis is completed when all of the sample gas has been passed through the analytical instrument 1 and discharged to the surroundings or to some other receiving station.

5 Although not shown in the drawing, the analytical instrument 1 includes a few valves in addition to sensors/-detectors. These valves have not been shown, however, since they do not assist an understanding of the present invention.

10 Figure 1 shows an additional refrigeration drier 30 and associated conduits 31 and 32. Such an apparatus set-up is used when wishing to start preparing a fresh gas sample, although the refrigeration drier 5 shown on the left of the Figure still dries and cleans. As will be seen from Figure 1, the conduit 29 is connected to a branch conduit 33 so as to 15 enable the air and helium mixture having a constant oxygen content can be delivered to a location upstream of the analytical instrument 1, more specifically to the conduit 14 that discharges into the analytical instrument 1.

15 The apparatus set-up illustrated in Figure 1 can be held in stand-by condition between the analytical occasions, by passing a dry helium-air mixture having a constant oxygen content through the external analytical instrument 1 while pure helium is passed "rearwards" through the adsorber-/desorber 10 in order to keep it clean.

20 In the apparatus illustrated in Figure 1, the original volume of sample gas freed from its volatile substance content and from the major part of its water vapour content leaves the system through the outlet conduit 15. It is not necessary to use a flow circuit of such length, but 25 the gas volume concerned may alternatively be caused to leave the flow circuit via the outlet conduit 19 or via the conduit 34 on the opposite side of the first switching valve 8.

25 As before mentioned, it is not always necessary to remove water vapour from the original volume of sample gas.

Whether or not water vapour shall be removed is dependent, among other things, on the method of analysis employed. When water vapour need not be extracted from the gas, all of the initial flow circuit shown in Figure 1 is removed and the 5 original gas volume is introduced into the inventive apparatus directly through the conduit 7 functioning as a supply conduit. In this case, the regulating unit 17 need not have or create as many functions, as will be evident from the foregoing.

10 The aforescribed apparatus set-up is managed manually to a large extent. In those instances when a specific type of sample gas shall be analysed, for instance day after day, in accordance with a certain analytical process, the sample preparation process and the metering 15 process according to the invention can be automated and computer-controlled in a relatively easy manner.

Example 1

Described below are tests carried out on headspace gas over paper in accordance with the invention and in 20 comparison with zero samples.

60 grams of computer printing paper (wood containing) having a grammage of 60 grams per m^2 was cut into strips of 20 x 200 mm and placed in a circular glass tube having a volume of 1500 ml and a length to diameter ratio of about 7:1 25 (sampling vessel), which had been flushed through with helium. The ends of the sampling vessel were equipped with closure valves of glass and PTFE (polytetrafluoroethylene).

It has been found that when paper samples are placed in a sufficiently long and narrow sampling vessel, 30 such as that described above, it is possible, after equilibrium between gas phase and solid phase, i.e. the paper phase, has been reached, to take out a gas sample containing equilibrium contents of the volatile constituents of the

paper, by passing a gas stream sufficiently slowly through the sampling vessel. The gas volume taken out should not exceed two-thirds of the volume of the sampling vessel.

After the volatile components of the paper have
5 reached their equilibrium contents in gas phase at the prevailing temperature, i.e. the ambient temperature, of 23.3°C, a stream of helium of constant regulated rate of flow (22 ml/min) was led from a pressurised gas cylinder into one end of the sampling vessel. Equilibrium gas sample was taken
10 out from the other end of the sampling vessel and treated in accordance with the invention in the following manner.

The inventive apparatus set-up shown in Figure 1 was used and the sample gas, i.e. 22.3 ml of moist gas per minute, was led through the conduit 2 to the initial
15 switching valve 3 and from there to the refrigeration drier 5 through the conduit 4. Subsequent to removing water, the sample gas was then passed through the conduit 6 to the valve 3 and from there to the first switching valve 8 through the conduit 7, and from there to the adsorber 10 through the
20 conduit 9. After removing the volatile substances, the gas was passed to the valve 8 through the conduit 11 and discharged from the system through the conduit 19. 1115 ml of moist gas (1100 ml dry gas) was taken out from the sampling vessel.

25 Seen from inside, the adsorber 10 comprised a deactivated glass tube having closed ends. The glass tube was enclosed in a brass cylinder which, in turn, was embraced by insulated resistance filament or wire, which enabled the sorbent to be quickly heated. The adsorber was surrounded by
30 metal plates in the form of Peltier elements which enabled the inner temperature of the glass tube to be regulated, primarily lowered. 70 mg of Tenax TA were used as the sorbent, Tenax TA being chemically poly-2,6-diphenyl-p-

phenylene oxide. The temperature was set to 0°C during the adsorption phase.

No inerting phase was used in the described test, since the sample gas was comprised substantially of helium 5 gas and not air, with its oxygen content.

The desorption phase was then applied, by passing helium from the regulating unit 17 to the first switching valve 8 via the conduit 18 at a rate of flow of 5 ml/min. The flow of helium was then passed through the conduit 11 to the 10 adsorber 10 which, at this stage, was heated to 180°C with the aid of said resistance wire and thereby converted to a desorber, wherewith the volatile substances were taken up by the flow of helium which left the desorber 10 through the conduit 9 which delivered the gas flow to the valve 8, 15 wherewith the gas flow was passed to the second switching valve 13 through the conduit 27 and to the infusion pump 16 through the conduit 28. A total of 50 ml helium was passed through this described path, meaning that the volatile substances were enriched in a gas volume of 50 ml at this 20 stage of the operation, as compared with the original sample gas volume of 1115 ml. The helium was driven through the system by drawing down the piston 25 in the infusion pump 16 at a specific speed and to an extent such that 50 ml gas, together with its volatile substances content were enclosed 25 in the infusion pump. The described modus operandi of the infusion pump 16 is referred to as aspiration.

In the tests described here, the analytical instrument 1 was a gas chromatograph designated Perkin-Elmer Sigma 300 B. The concentration and injection system comprised 30 JATEC C1U1D with cryofocusing in a refrigerating trap cooled with liquid nitrogen. Flame ionization detector was used parallel with the mass spectrometric detector Finnigan ITD. The chromatography computer system Scientific Software EZChrom was used. The column used was comprised of deacti-

vated silica having a length of 60 m and an inner diameter of 0.32 mm, and was coated with 1.0 micron of methyl polysiloxane DB-1, which was immobilized and cross-linked. Helium was used as the carrier gas in the actual gas chromatograph, with a rate of flow of 3.4 ml/min. The column temperature program was 30-200°C with 4°C/min, 200-250°C with 10°C/min and 3 minutes isothermal at 250°C.

The gas sample present in the infusion pump 16 was metered to or injected in the gas chromatograph 1, by moving the piston 25 upwards at a speed such that 10 ml of gas sample were delivered to the refrigerating trap in the injection system of the gas chromatograph per minute through the conduit 28, the second switching valve 13 and the conduit 14. The cryofocused sample was injected by leading the carrier gas (helium) through the refrigerating trap, which was quickly heated to 150°C.

The gas chromatographically separated components were quantified with the aid of the flame ionization detector, calibrated with n-nonane, and known substance specific correction factors relative to n-nonane. The mass spectrometer was used for an identity check of the quantified components, i.e. the volatile substances.

The results obtained with the analysis are given below in Table 1.

It is important to note that all of the parts of the sample processing apparatus according to the above that were in contact with the sample gas were comprised of glass, deactivated silica, PTFE (polytetrafluoroethylene) or FEP (hexafluoropropylene polymerized with tetrafluoroethylene).

The amount of water extracted from the original gas sample in the refrigeration drier 5, which operated at a temperature of -15°C during drying of the gas sample, was determined when regenerating the drier 5 in accordance with prevailing technology, by capturing the molten ice, i.e. the

water, in a glass freeze trap which was cooled with liquid nitrogen. The freeze trap included sealing end-plugs. The amount of water was measured gravimetrically and it was found that 5.5 mg water was obtained from 500 ml sample gas, which 5 is the amount expected from the paper sample at an ambient temperature of 23.3°C and a relative air humidity of 50%.

A comparison test was carried out on the same paper and with a paper sample initially prepared in the same manner as that aforescribed, without enriching the volatile 10 substances in the original gas sample, here designated the zero sample.

The outlet end of the earlier described sampling vessel was provided with a branch pipe. 100 ml of moist gas (98.6 ml dry gas) from the outflowing sample gas was sucked 15 via parts of the apparatus set-up shown in Figure 1 down into the infusion pump 16 at a rate of 15 ml dry gas per minute, while the remaining part of the sample gas flow was removed as an overflow through said branch pipe.

This 100 ml of moist gas was passed through the 20 conduit 2 to the initial switching valve 3 and from there to the refrigeration drier 5 through the conduit 4, the temperature of said drier being -15°C. Water was recovered in the refrigeration drier 5 in the form of ice and the gas sample freed from water was passed through the conduit 6 to 25 the initial switching valve 3, through said valve and from there through the conduit 7 to the first switching valve 8, through the conduit 27, through the second switching valve 13, and through the conduit 28 to the infusion pump 16.

The dry gas, measuring 98.6 ml, was metered to or 30 injected into the gas chromatograph 1 in the earlier described manner.

The result of this analysis is given below in Table 1.

The theoretical enrichment factor for this test

carried out in accordance with the invention is

$$\frac{1115 \text{ ml}}{50 \text{ ml}} = 22.3.$$

Table 1

5	Volatile substance	Boiling point °C	Conc. in gas phase nanogram/l		Enrichment factor
			Zero sample	Enriched sample	
	ethanal	20.8	189	3430	18.2
	n-pentane	36.1	104	2240	21.6
	acetone	56.2	510	9840	19.3
	n-butanal	75.7	24	506	21.1
10	2-propanol	82.4	990	17100	17.3
	n-pentanal	103.0	120	2880	23.9
	toluene	110.6	25	601	24.1
	n-hexanal	128.3	560	11600	20.7
	n-heptanal	152.8	20	409	20.2

15 The test carried out in accordance with the invention has resulted in enrichment factors that lie relatively close to the theoretical enrichment factor of 22.3, essentially regardless of the measured boiling point of the volatile substances.

20 The slightly lower enrichment factors of very polar, hydrophilic, molecules such as 2-propanol, ethanal and acetone can be ascribed to losses in the refrigeration drier 5, the flow and temperature parameters of which were not optimized.

25 The enrichment factors were higher than the theoretical enrichment in two instances. It is probable that measurement errors crept on these occasions. The zero sample is the first to be questioned in this respect, since, as before mentioned, it is more difficult to obtain a true

analysis result from the analytical instrument when the gas sample has a low volatile substance concentration in comparison, e.g., with a gas sample that has a volatile substance concentration that is twenty times greater or more 5 than the gas sample concentration.

It can be added in conclusion, that in both of the aforescribed tests, that is including the zero test, there has been used a central device in the inventive apparatus, i.e. the infusion pump 16, for metering the sample gas to the 10 analytical instrument. The advantage gained when using such an infusion pump for this work is not as pronounced with a gas chromatograph as the analytical instrument as in the case when the analytical instrument is a so-called electronic nose for instance.

CLAIMS

1. A method of enriching volatile substance or volatile substances from a gas flow that has already been generated, and metering the volatile substance or volatile substances to an analytical instrument in a limited gas volume, **characterized** by either sucking or pressing the gas flow via a first switching valve to an adsorber in which the volatile substance or volatile substances is/are adsorbed, and causing the gas flow freed from said substance or substances to leave the system via at least said first switching valve;

causing a controlled amount of inert gas to flow via the first switching valve to the adsorber, which is heated, with the aid of an infusion pump (aspiration), and through said adsorber (thermal desorption) while taking-up the volatile substance or volatile substances, again via the first switching valve and via a second switching valve to the infusion pump; and delivering the inert gas together with its volatile substance or volatile substances content to the analytical instrument via said infusion pump (injection) and said second switching valve.

2. A method according to Claim 1, **characterized** by refrigeration drying the gas flow in an initial treatment stage so as to free said gas from a minor or a major part of its water vapour content.

25 3. A method according to Claim 1 and 2, **characterized** in that when no oxygen may be present in the thermal desorption process or subsequent thereto, an inert gas is caused to flow through the adsorber, prior to said adsorber being heated, so as to displace any 30 oxygen that is present, the inert gas and its oxygen content

being caused to leave the system via at least the first switching valve.

4. A method according to Claims 1-3,
5 **characterized** by delivering an oxygen containing gas to said limited gas amount immediately upstream of the analytical instrument or in said instrument.

5. A method according to Claims 1-4,
5 **characterized** by using helium or nitrogen as the inert gas.

10 6. Apparatus for enriching a volatile substance or volatile substances from a gas flow that has already been generated, and metering the volatile substance or volatile substances to an analytical instrument (1) in a limited gas quantity, **characterized** in that the apparatus includes a first gas flow circuit that comprises conduits (7, 11, 9), a first switching valve (8), an heatable adsorber (10) where the volatile substance or volatile substances is/are adsorbed, an outlet for cleansed gas flow (19, 34, 15) and means for driving the gas flow through the flow circuit;
15 a second flow circuit for a limited quantity of an inert gas that functions as a vehicle for the volatile substance or the volatile substances, said second circuit comprising a regulating unit (17) for said inert gas and another gas, conduits (18, 11, 9, 27, 28), said first switching valve (8) the heated adsorber functioning as a desorber (10), a second switching valve (13), and an infusion pump (16) which drives the inert gas through the flow circuit; and a third flow circuit for delivering the inert gas and its volatile substance or volatile substances content to the analytical instrument (1), said third flow circuit comprising conduits
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(28,14), the second switching valve (13) and said infusion pump (16).

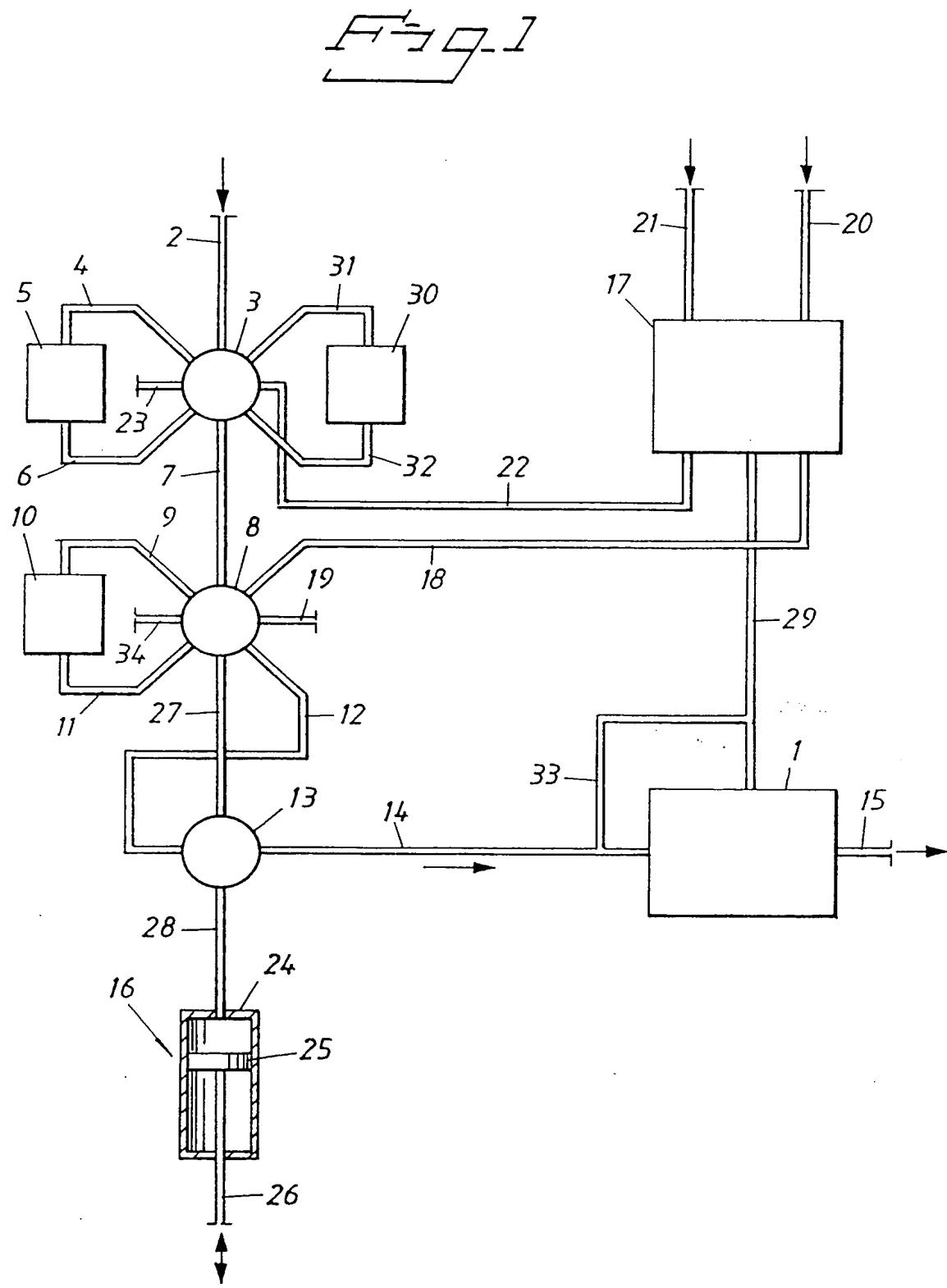
7. Apparatus according to Claim 6,
5 characterized in that the apparatus is
supplemented with an initial flow circuit for extracting
water vapour from said gas flow, said initial flow circuit
comprising conduits (2,6,4), an initial switching valve (3),
at least one refrigeration drier (5), and said gas flow drive
means, which drives said gas flow through the initial flow
10 circuit.

8. Apparatus according to Claim 7,
15 characterized in that said apparatus includes an
inlet conduit (22) and a regulating unit (17) for delivering
cleansing gas, for instance air, and an outlet conduit (23)
for removing water condensate and/or water vapour from the
refrigeration drier (5) and the flow circuit subsequent to
treatment of the gas flow.

9. Apparatus according to Claims 6-8,
20 characterized in that the apparatus includes a
regulating unit (17) and a conduit (29, 33) for supplying
oxygen containing gas, wherein said conduit opens into the
conduit (14) that is connected to the analytical instrument
(1), or delivers the gas into the analytical instrument (1)
itself.

25 10. Apparatus according to Claims 6-9,
30 characterized in that the means which drives the
gas flow through the flow circuit or flow circuits concerned
is comprised of a pump mounted in the external analytical
instrument (1) or in a conduit (15) that extends out from
said instrument.

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SUBSTITUTE SHEET (RULE 26)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 99/01058

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: G01N 1/40, G01N 1/22

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: G01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 5092156 A (GABOR MISKOLCZY), 3 March 1992 (03.03.92), column 4, line 25 - column 5, line 28 --	1-10
A	US 5395589 A (SABATINO NACSON), 7 March 1995 (07.03.95), column 6, line 37 - line 52; column 12, line 44 - column 14, line 15 --	1-10
E,A	WO 9857141 A1 (BIOSENSOR APPLICATIONS SWEDEN AB), 17 December 1998 (17.12.98), page 14, line 10 - page 15, line 3 -- -----	1-10

 Further documents are listed in the continuation of Box C. See patent family annex.

* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- "&" document member of the same patent family

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INTERNATIONAL SEARCH REPORT

Information on patent family members

28/09/99

International application No.

PCT/SE 99/01058

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